Development of Sensors for Automotive PEM-based Fuel Cells

DOE Agreement DE-FC04-02AL67616

United Technologies Research Center

Nancy Garland - DOE

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UTC Fuel Cells
A United Technologies Company

NEXTECH MATERIALS

ATMI

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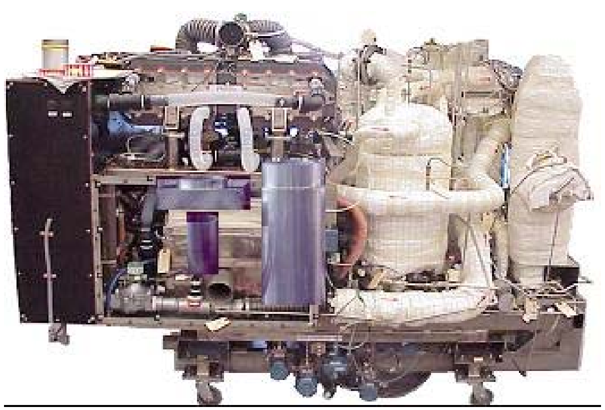
DOE Hydrogen and Fuel Cells 2004 Annual Merit Review

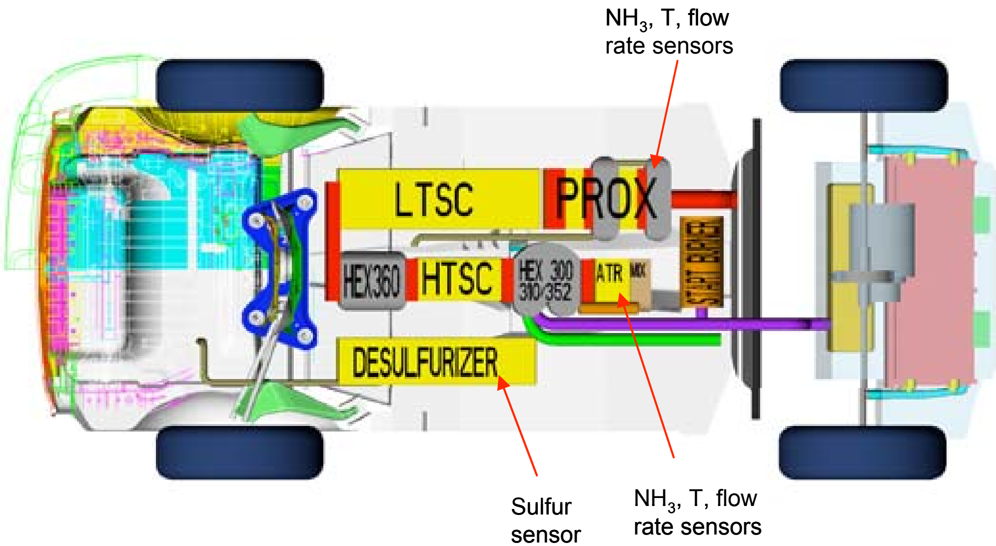
May 26, 2004



UTC FC Series 200 - 50 kW PEM

Sensors for Automotive PEM Fuel Cells – Objectives

Develop a technology and commercial supplier base for physical and chemical sensors required to optimize the operation of PEM fuel cell power plants for automotive applications with path to low cost (<$20 / sensor) at 500k qty.



- Chemical sensors
  - –Process streams: before, in, and after reformer, before and in fuel cell stack: CO, H_2, O_2, H_2S, NH_3; Safety [H_2].
- Physical Sensors
  - –Temperature, pressure, relative humidity, flow, ΔP

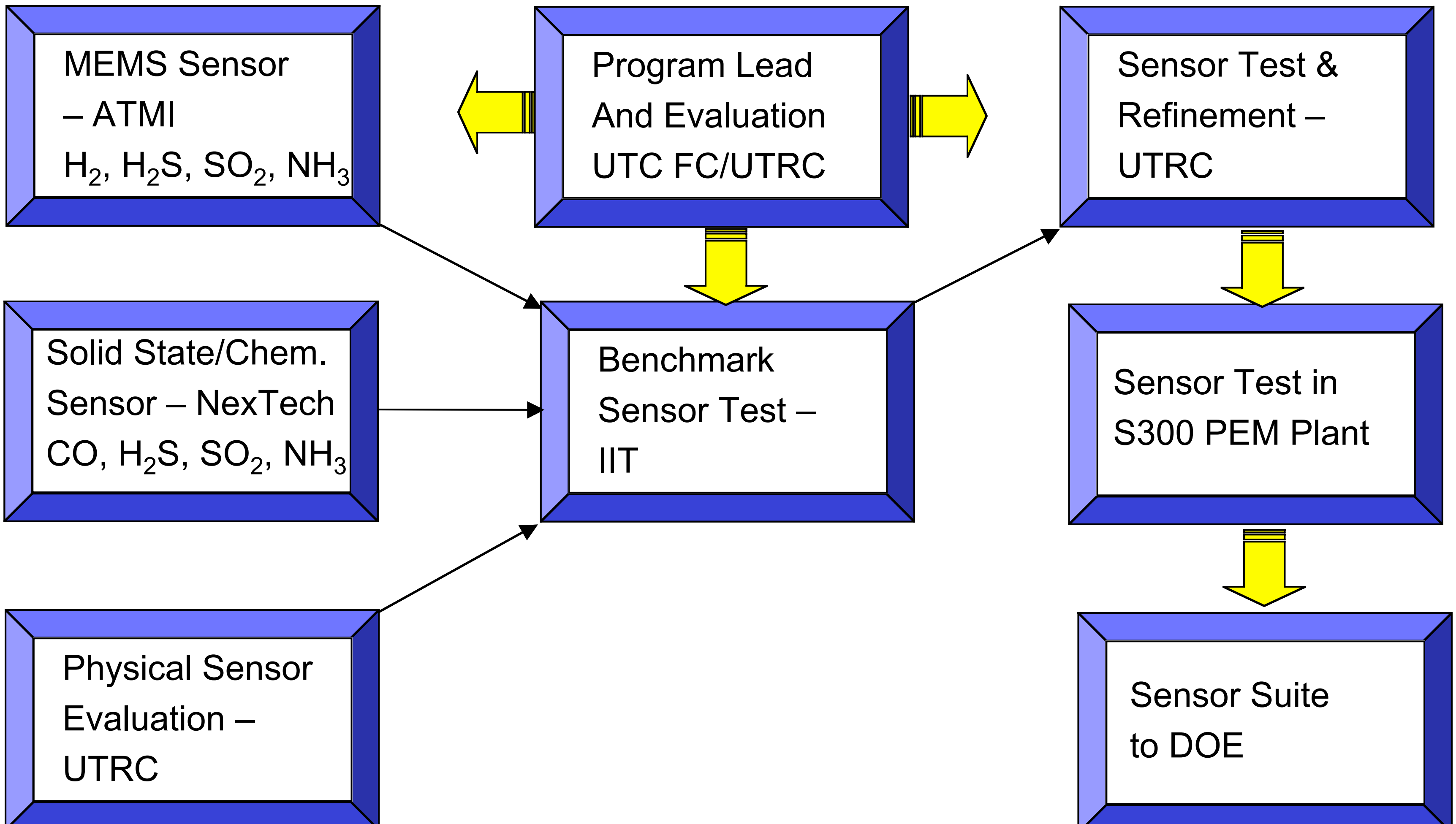
Sensor Program Team Responsibilities

- Sensor development program utilizes a team approach
  - UTRC for physical and chemical sensor evaluation and program coordination
  - Illinois Institute of Technology (IIT) for chemical sensor evaluation
  - Advanced Technical Materials (ATMI) for MEMS sensor development
  - NexTech Materials for electrochemical and solid state sensor development

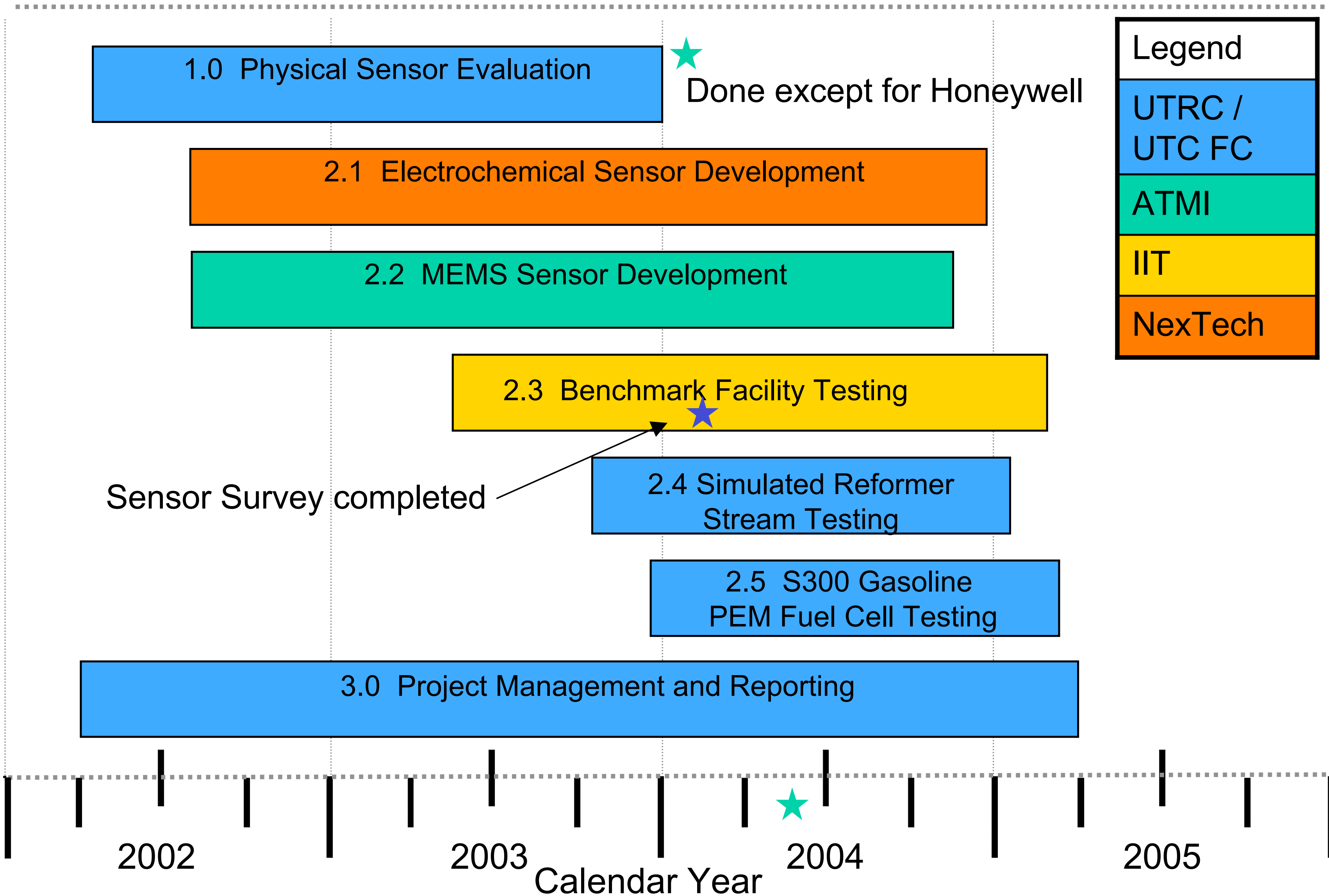
Team Member	T	ΔP	RH	flow	O_2	CO	H_2	SO_2	H_2S	NH_3	Technological Expertise / Responsibility
UTC FC	X	X	X	X	X	X	X	X	X	X	Testing on S300 Breadboard
UTRC	X	X	X	X	X	X	X	X	X	X	Testing in reformate simulator
ATMI							X	X	X	X	Develop Using MEMS Silicon Microhotplate
IIT	X		X		X	X	X	X	X	X	Testing in Benchmark Facility
NexTech						X		X	X	X	Develop Using Solid State Electrochemical

Sensor Program Team Structure

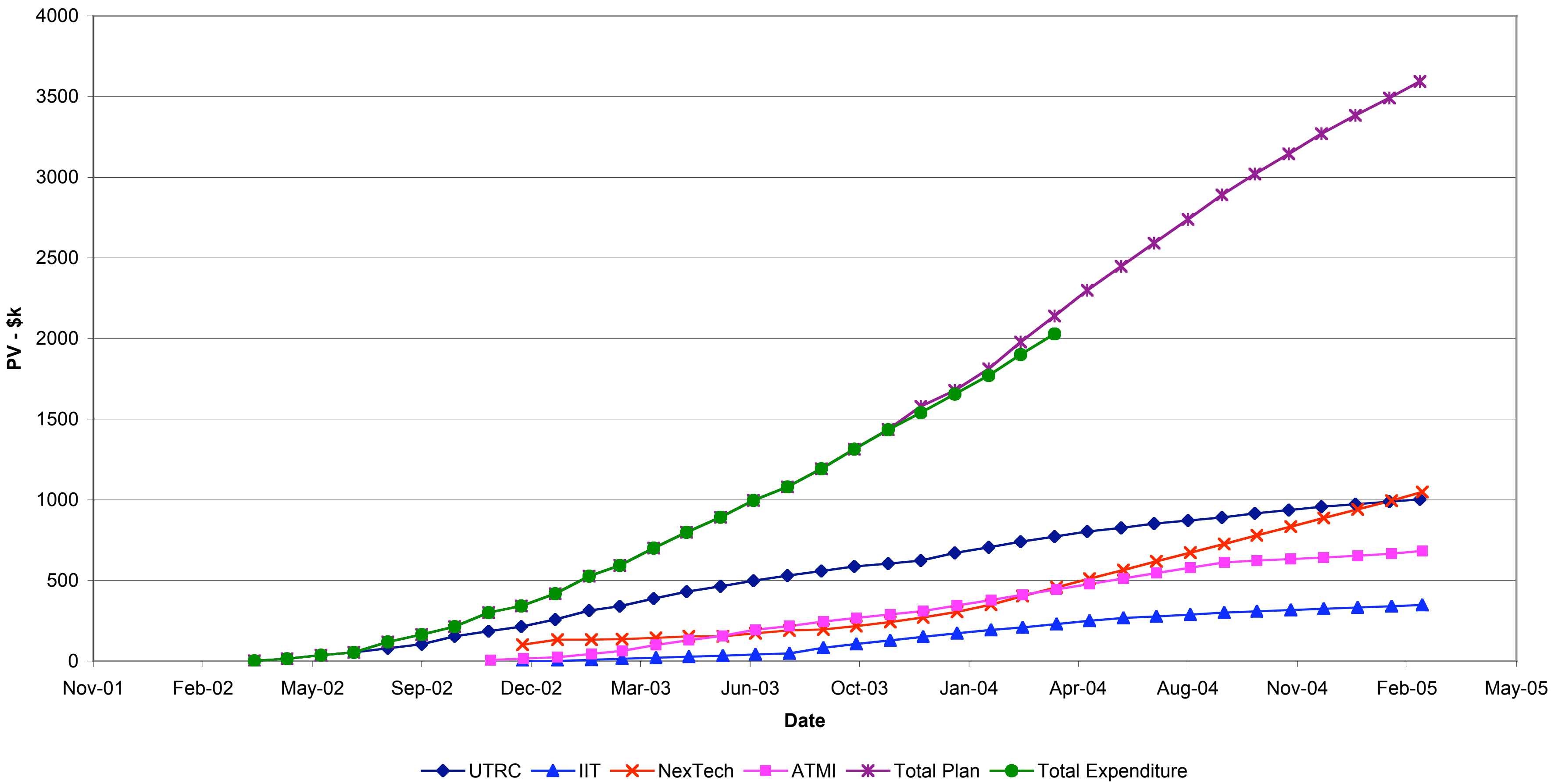
- Continuous interaction among team members
- ATMI, NexTech develop sensors, IIT and UTRC test and aid in optimization



Sensors for Automotive Fuel Cells Plan



Sensors Program Financial Status



- Total cost: $3.7MM; DOE cost: $3.0MM (80%) UTC Cost Share: $0.7MM (20%)
- Total expended to date: $1.6MM
- Duration: April 2002 – March 2005

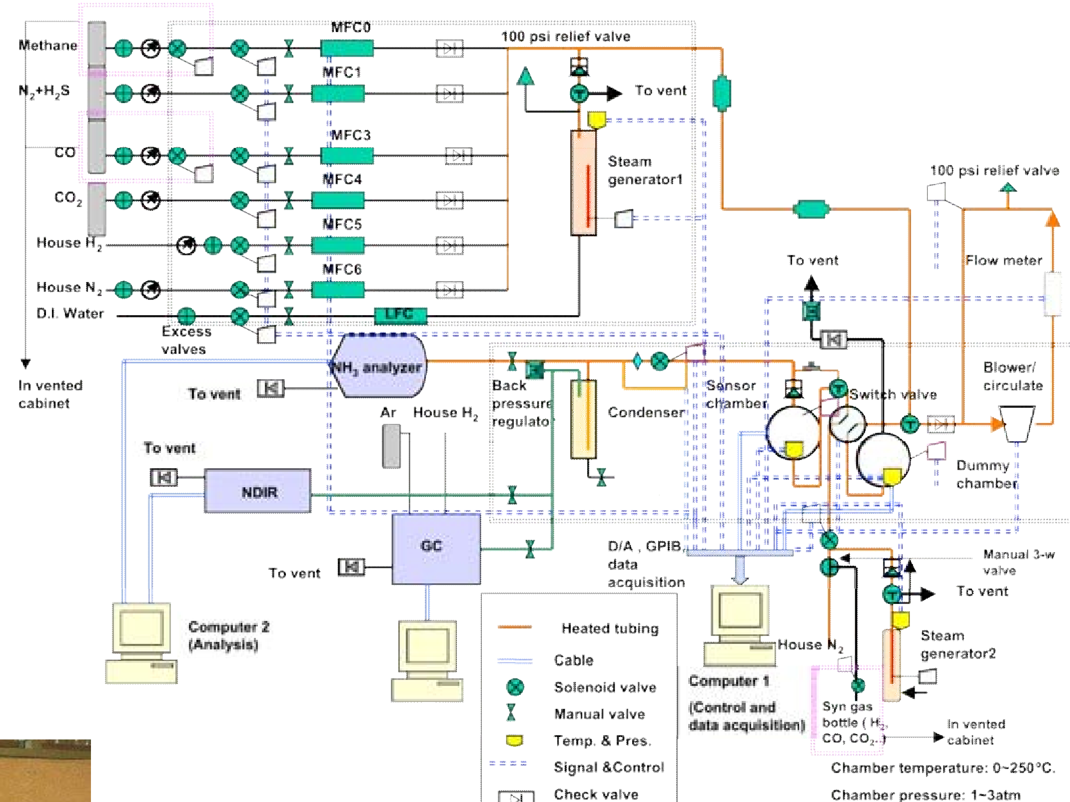
H_2 Safety Issues Associated with Project

- Use of H_2 in laboratory environment
  - Flammable gas detectors located in laboratory; relay opens and turns off power to solenoid valves on H_2 supply at 10% of LEL
  - LabView-based control program senses alarm, shuts off all other gases and purges all gas lines with N_2
  - All valves used in experiment are explosion-proof
  - Pressure relief valves used in all piping to prevent over-pressurization of components
- Sensor technology
  - Heated sensing elements can provide an ignition source; therefore the detection element must be separated from the gas stream by a flash-arrestor (porous plate) to prevent ignition of the bulk gas

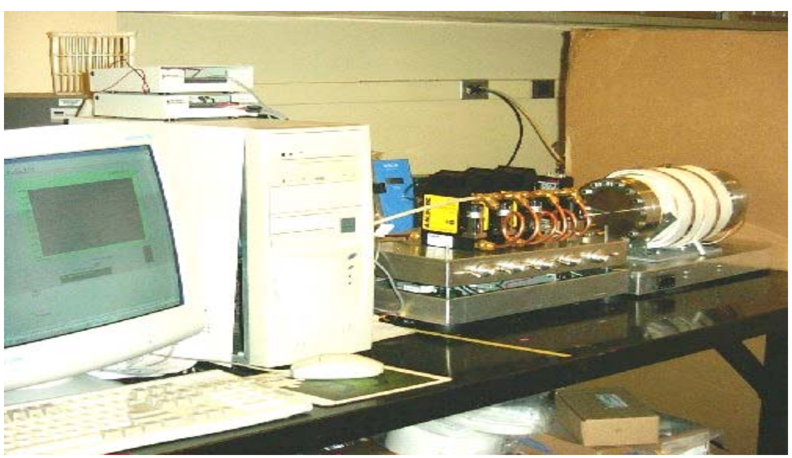
PEM Fuel Cell Gas Stream Simulators at UTRC & IIT

Both test rigs operate under LabView control for 24/7 operation (data acquisition and test matrix completion)

Test chamber
(25 - 450°C)
Pressure: 1-4 atm



UTRC test rig with dual chambers



IIT test rig

Sensor Evaluation Status at UTRC

Lei Chen and Brian Knight

- Physical Sensors
  - Sensors for T, P, ΔP, Relative Humidity (RH), and Flow evaluated in PEM fuel cell simulator in near-condensing flow regime
- State-of-the-art physical sensors meeting program needs selected
- Chemical Sensors
  - First round of sensor testing and qualification completed
  - Multiple H_2 sensors evaluated for sensitivity, selectivity, and performance
  - Possible extension of the testing effort beyond April 2005 being considered in order to accommodate field testing requested by Honeywell

Physical Parameter Sensors Results

•UTRC researched and tested multiple physical sensors; most promising tabulated below

Sensor	Operating Principle	Positive Attributes	Development Needs
Temperature	Thermistor	0 to 250 °C, -40 to 750 °C	Response time needs improvement
Pressure	Strain gauge (Druck)	Silicon based IC compatible fabrication.	May be mass produced and miniaturized
RH	Polymer capacitive (Panametrics)	0 to 180 °C, 0-100% RH	Improve recovery from condensing flow regime
Flow	Thermal dissipation	Most cost effective	Response fluctuation due to condensation

Benchmark Testing of Viable Sensor Technologies

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Joseph R. Stetter, William R. Penrose, William Buttner, and Kapil Gupta

- IIT evaluated over 70 H_2 sensing technologies
- Tiered approach used to evaluate sensor technologies
  - Gas concentration, operating temperature, water vapor pressure
  - Effect of pressure, other background gases
  - Long-term testing
- Hydrogen Sensors (Reformer)
  - -H2 Scan, Makel Engineering, ATMI, KSC NASA
- Hydrogen Sensors (Safety Application)
  - -H2 Scan, Applied Sensors, Makel Engineering, ATMI, Figaro, Transducer Technology, Inc., Argus Group, Nemoto Environmental Technology, Applied Nanotech
- Carbon Monoxide Sensor
  - -NexTech Materials

(Sensors currently available are listed in blue)

Process for Selection of Viable Sensor Technologies

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Literature search and review (for fuel cell sensors and H_2/CO sensors)

↓

Researched and short listed tentative companies, based on our requirement specifications, vendor products and application

↓

Contacted the companies and sent out sensor survey templates

↓

Evaluated the survey responses and accordingly sent out formal invitations for evaluation of sensors

↓

Now acquiring sensors- NDAs/other formalities

Testing acquired sensors and updating Sensor research Database
Intelligent Optical Systems, NASA/KSC/ASRC, NGK

Example of Shared Sensor Testing User Facility Data

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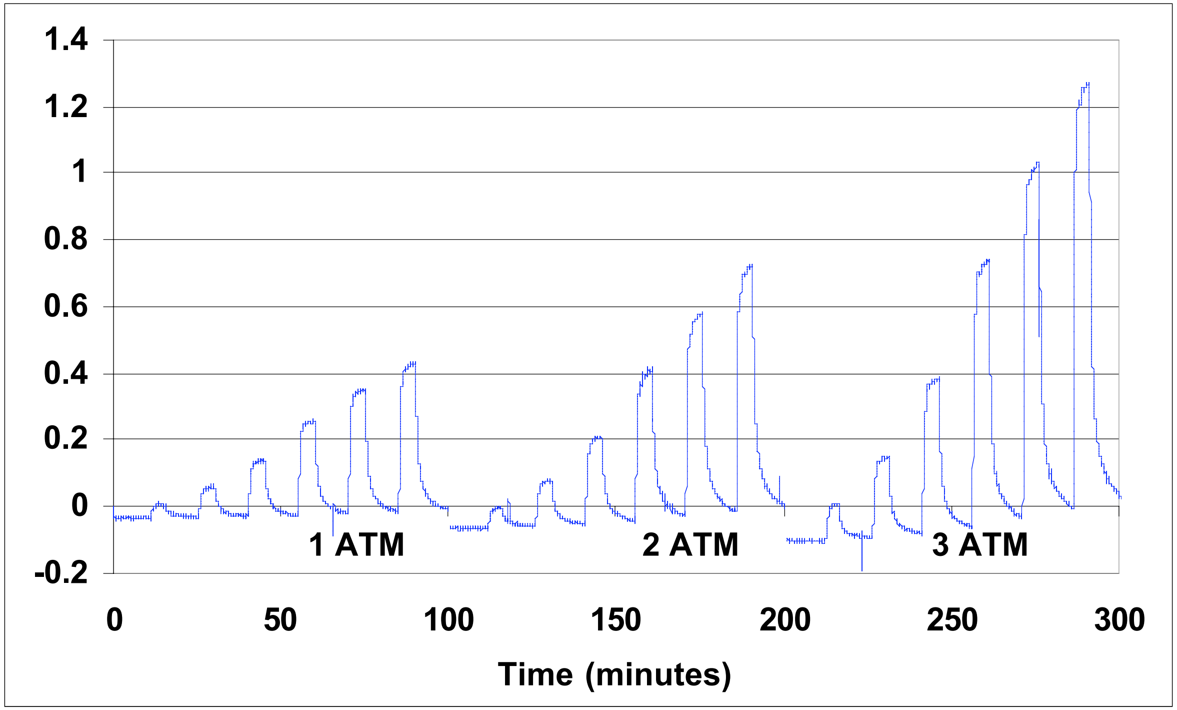
SSTUF: Hydrogen Sensor Response (0.5 to 8%) in air



P_{H2} Dependence (next slide)

Single Data Run

- Sensitivity Curves obtained for different pressures at 22^{o}C
- Automated Pressure Control, Flow Control and Concentration
- Capabilities also include Temperature Control and Humidity Control

Results of IIT H_2 Safety Sensor Testing in Air

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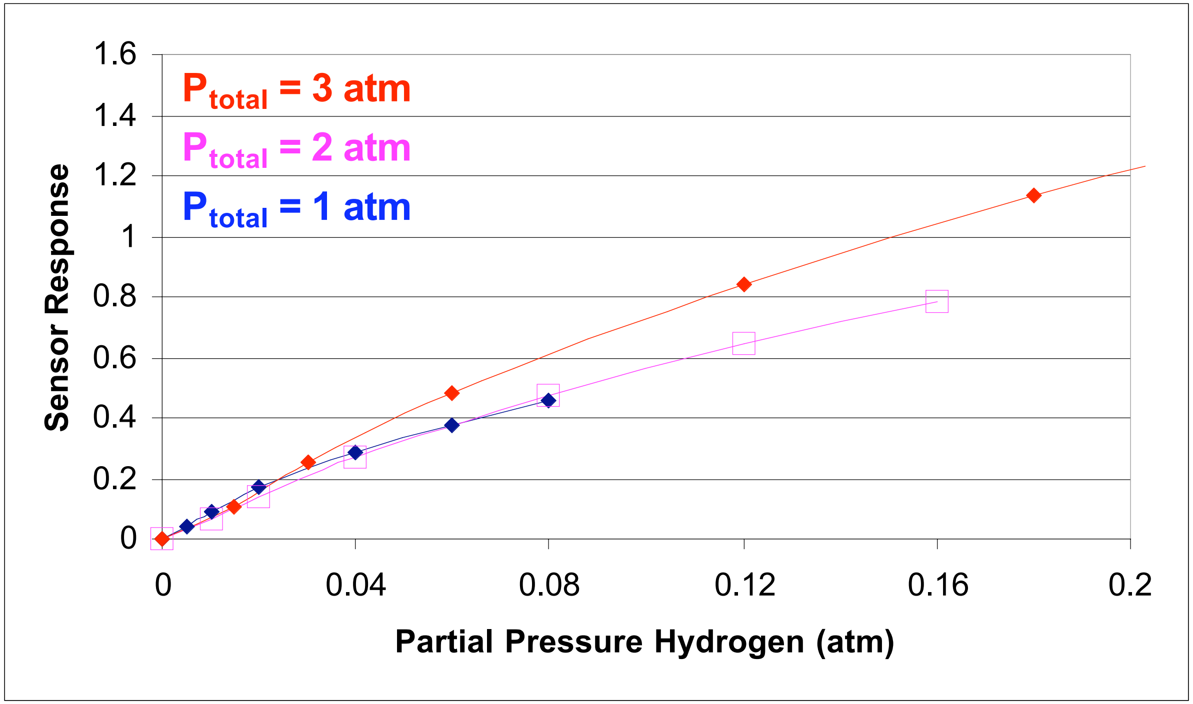
Hydrogen Sensor Response (0 to 0.2 atm) in air



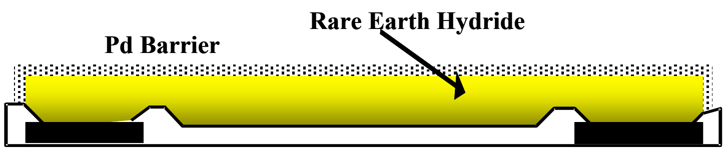
Sensor Sensitivity is often controlled by Partial Pressure of H_2 (not $\%H_2$)

MEMS Sensor Development
Task 1a Safety Sensor in Ambient Air

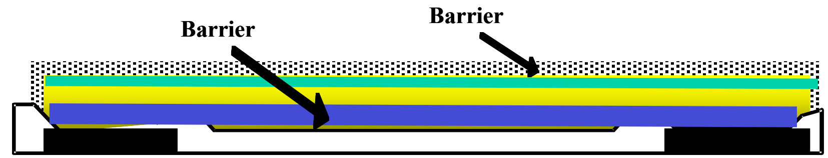
Ing-Shin Chen, Phil Chen, F. DiMeo, Jeff Neuner, Andreas Roehrl, Jim Welch

- Targets
  - [H_2]: 0-10%; Temp: –30 to 80°C, Response time: < 1 s; Humidity: 10-98%; Selectivity from hydrocarbons; Accuracy: 5%; Lifetime:5 yrs
- Approach
  - Fundamental materials engineering and process control
  - Optimization of operating conditions

Microhotptate Platform

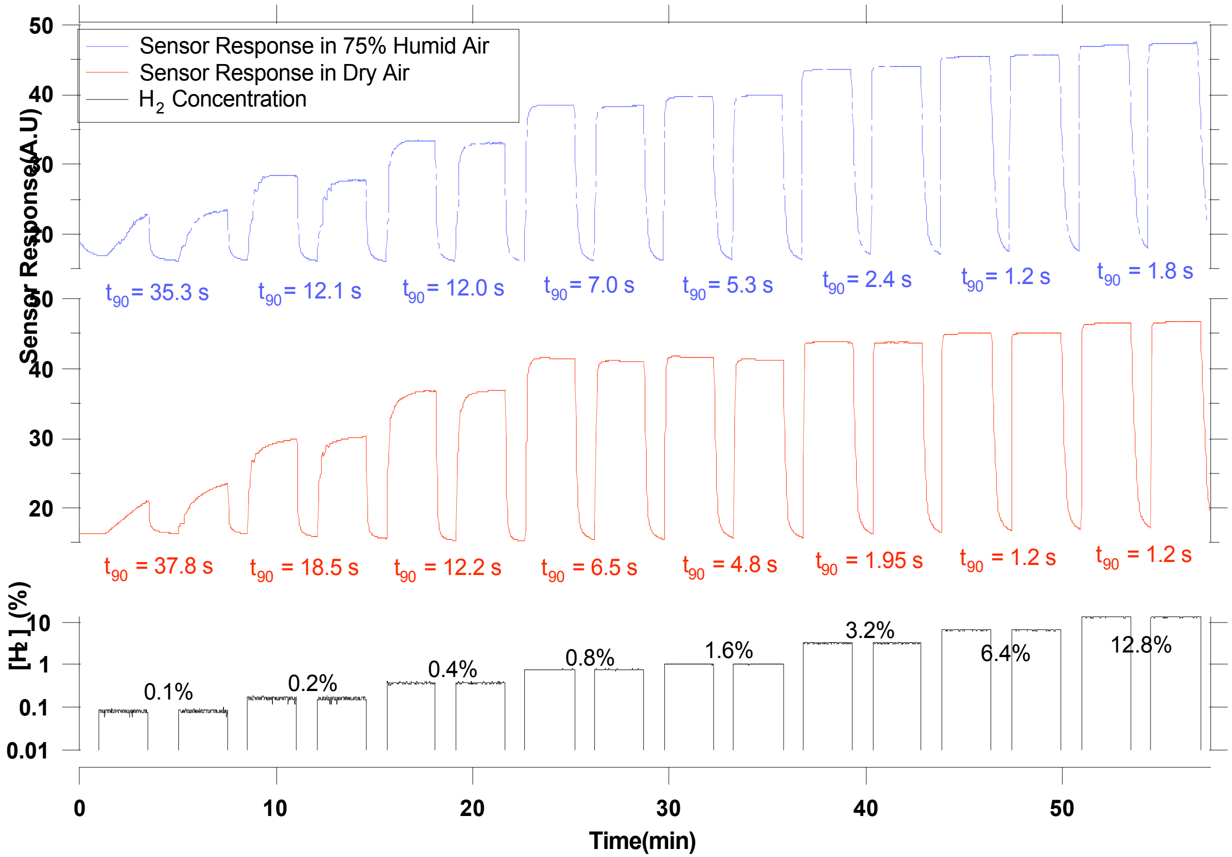


Microhotptate Platform



- Accomplishments
  - Developed and tested alpha, beta systems
  - Demonstrated performance against performance targets
  - Delivered alpha prototypes for IIT, UTRC for evaluation

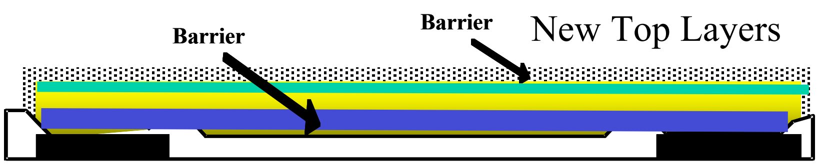
MEMS Sensor Development
Task 1a: Safety Sensor in Ambient Air



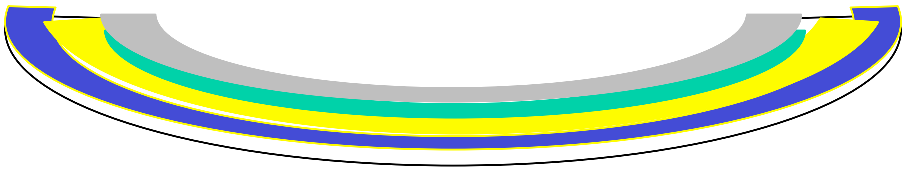
- Performance Demonstrated to date
  - $[H_2]$: 0-12.8%; Operating Temp: ~80^{o}C,
  - Response time: < 2 s @ 4%, 1.2s @ 6%
  - Environment: 0–75% RH;

MEMS Sensor Development
Task 1b Pre Stack Monitor

- Targets
  - $[H_2]$: 1-100%; Temp: 70- 150°C; Response (T_{90}):0.1-1 s; Environment: 1-3 atm total pressure, 10-30 mole % water, total H_2, 30-75%, CO_2, N_2 Accuracy: 1-10 % full scale
- Approach
  - Materials modifications of safety sensor design
  - Exploration of different transduction modes.



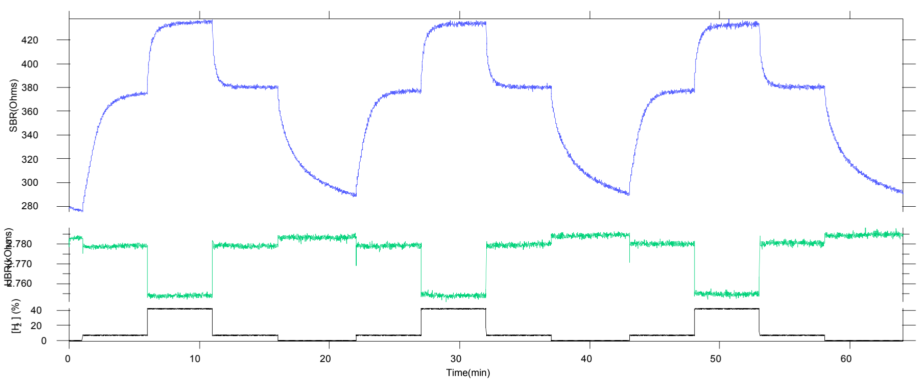
Microhotptate Platform

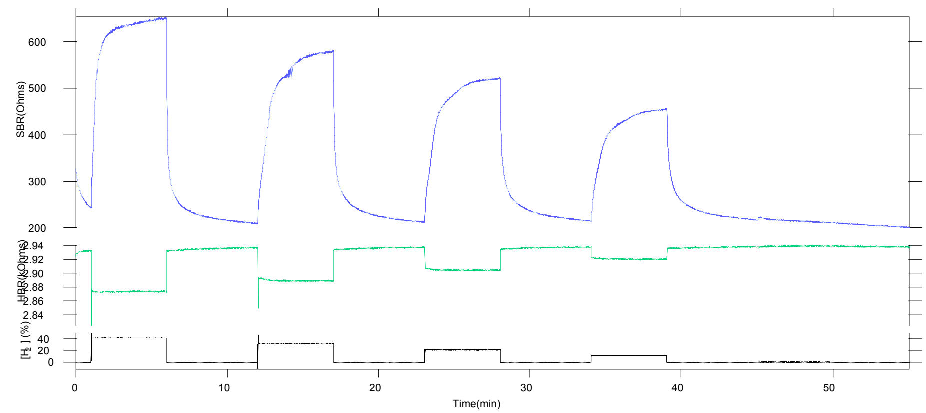


Piezo Resistive Transduction

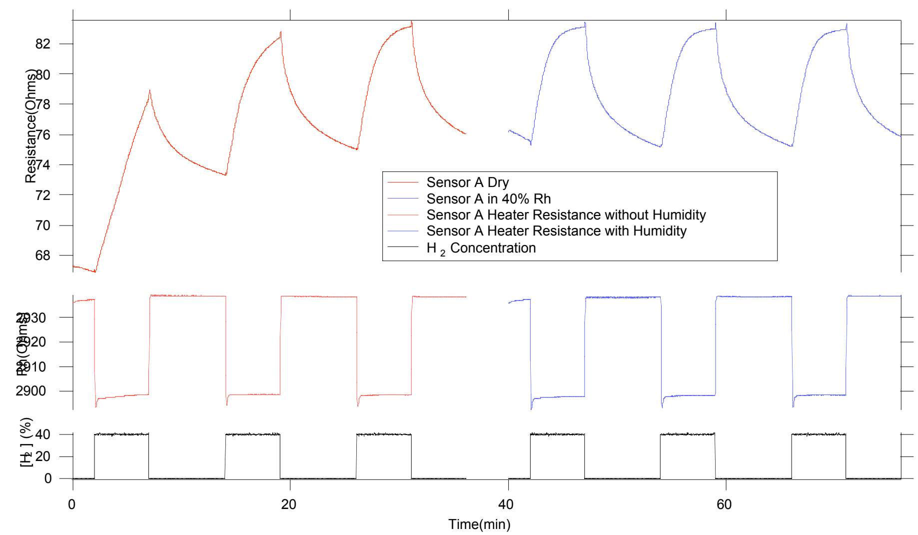
- Accomplishments
  - Fabricated new materials combinations
  - Investigated new transduction methods
  - Delivered alpha prototypes to UTRC

MEMS Sensor Development
Task 1b Pre Stack Monitor





- Performance in Dry N_2
  - 0-4-40% H_2
    - 37 sec t90 0 - 4%
    - 2 sec t90 4 - 40%
  - 40 to 10% H_2
    - 31.8 sec 0-40%
- Performance in 70% RH
  - Similar to dry N_2



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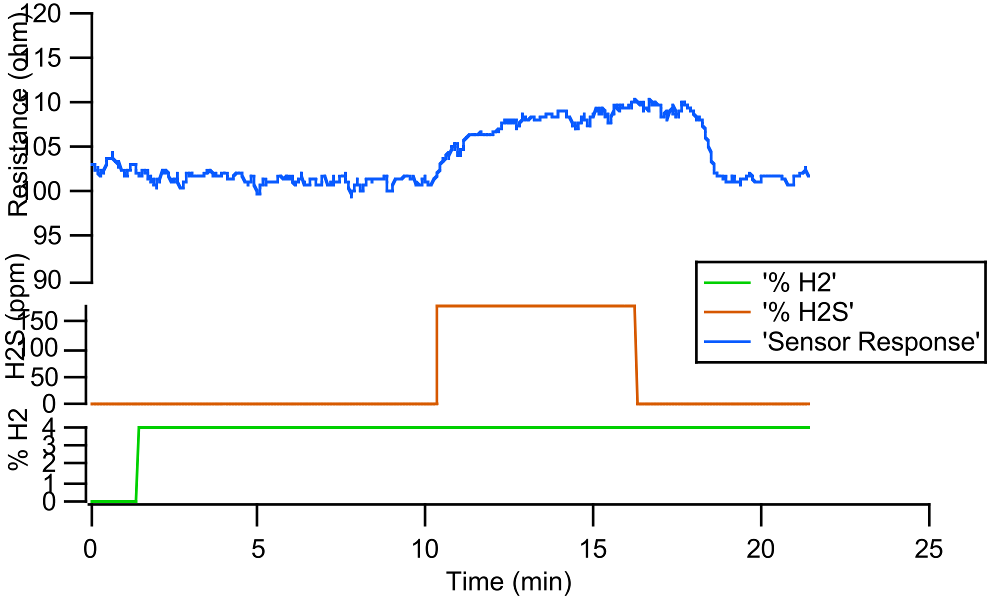
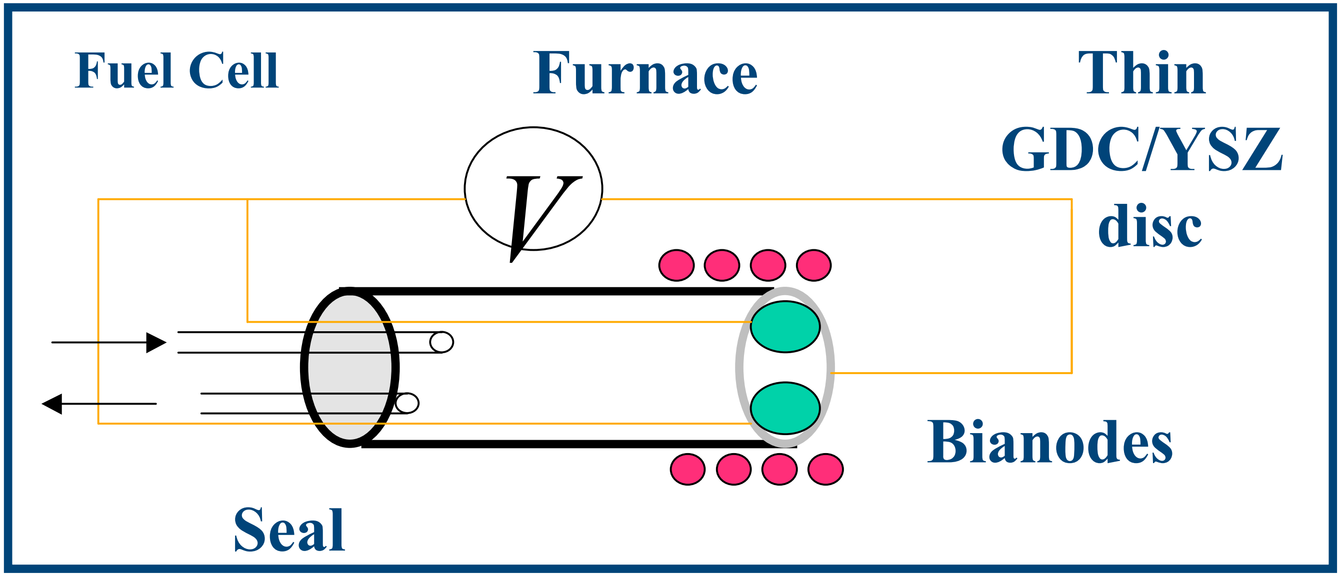
MEMS Sensor Development
Task 2 H_2S Sensor Development

- Targets
  - Temp: 400°C; Range: 0.05 ppm -0.5 ppm; Response time: < 1 min at 0.05 ppm; Environment: H_2,CO, CO_2 H_2O
- Approach
  - Ultra thin (< 50nm) metal film deposition on micro hotplate platform
- Accomplishments
  - Demonstrated first sensor response to H_2S
  - 50 nm film responds to H_2S
    - 160°C, 4% H_2/N_2,
    - 20% RH,
    - 180 ppm H_2S

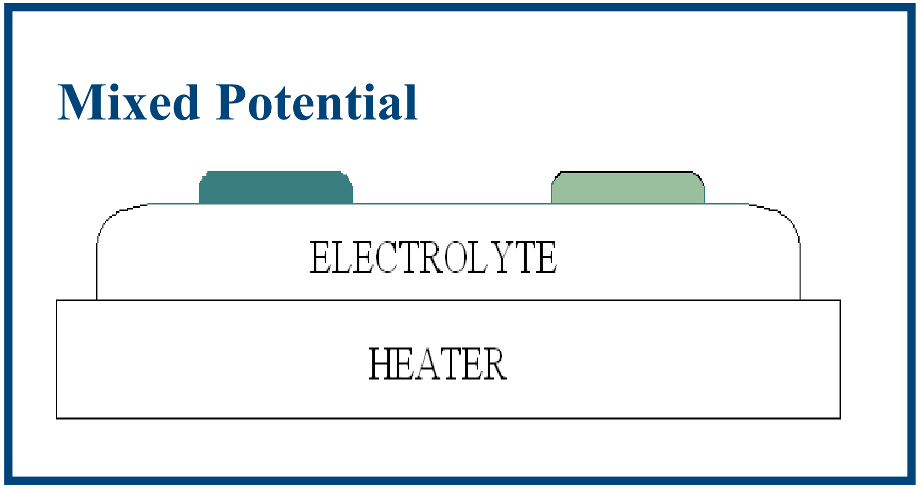


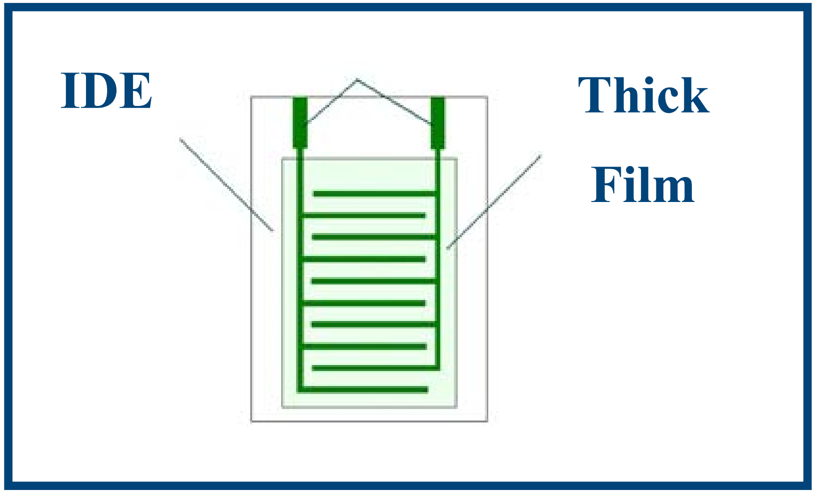
NexTech Materials Sensor Development

Scott L. Swartz, Ph.D. (P.I.), Chris Holt, Todd G. Lesousky



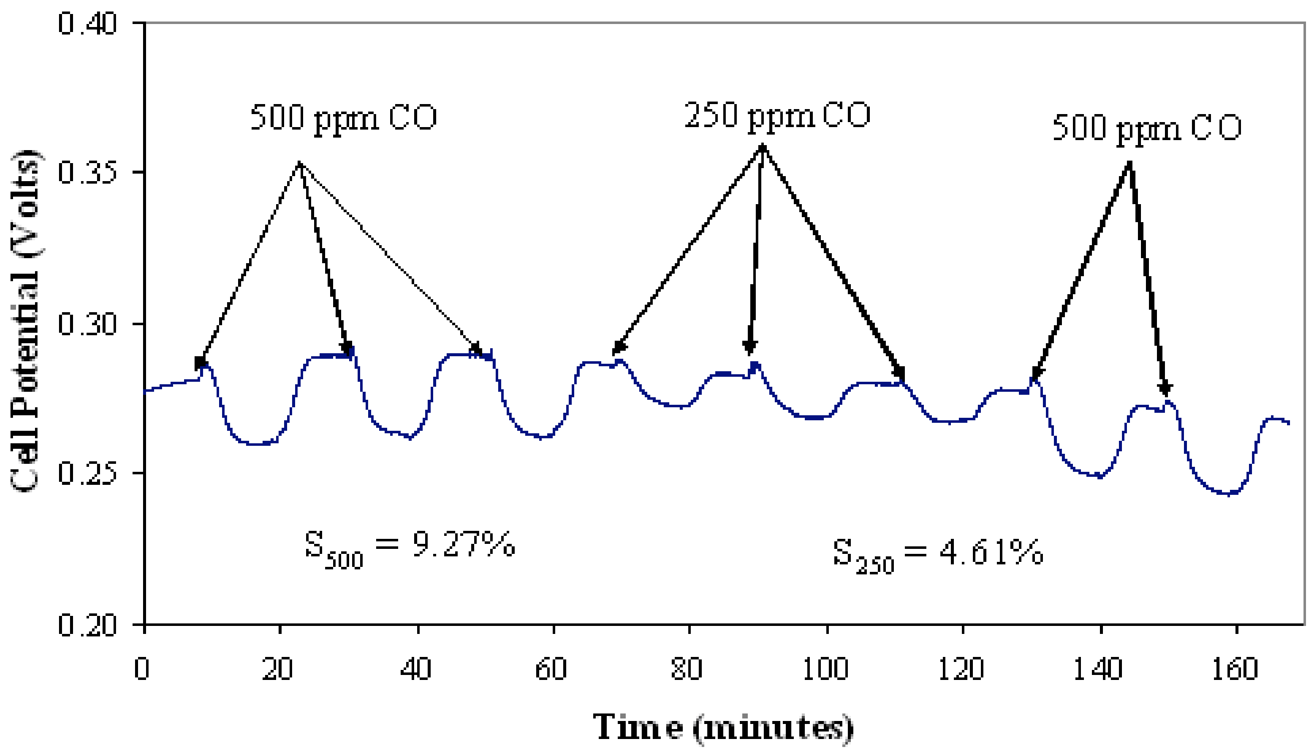
Sensor Platforms





NexTech Sensor Development
Task 2.1.1 Miniature SOFC Fuel Cell Sensor

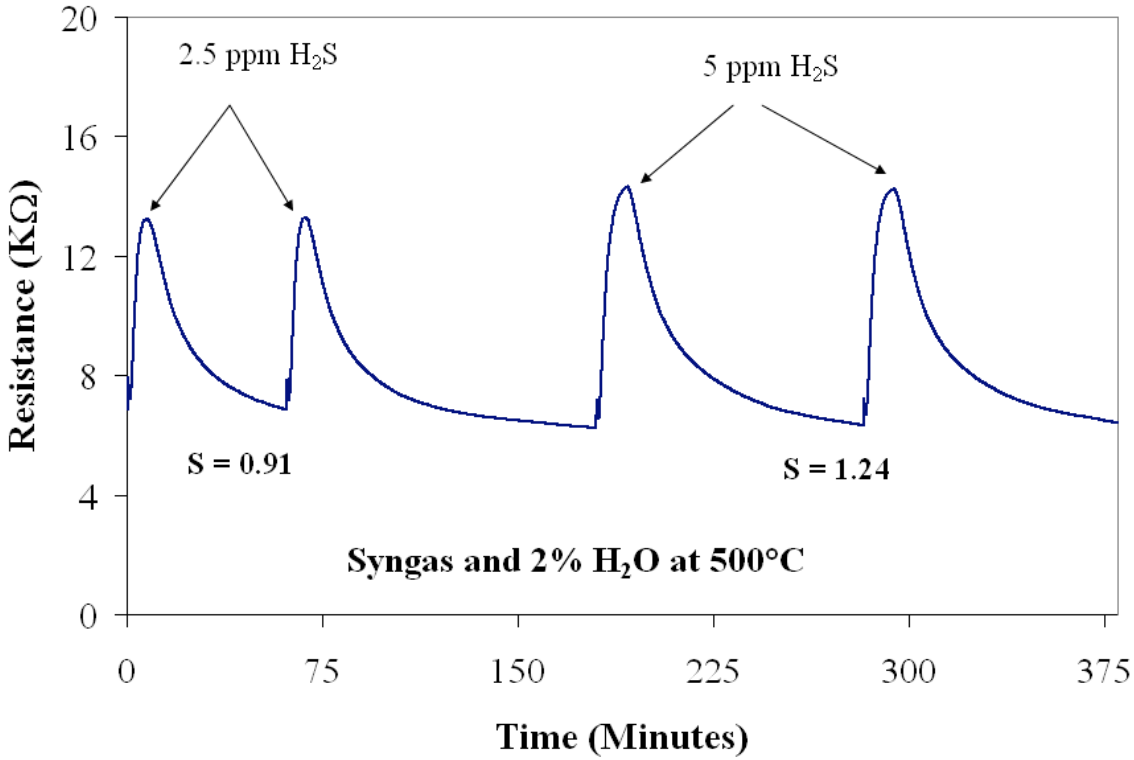
NexTech Materials



- NexTech's SOFC sensor technology with electrodes engineered to respond to CO show reversible and quantitative response to CO in wet N_2/H_2.
- Future work will focus on schemes to improve sensitivity for 0-100ppm CO range and testing cross-sensitivity to alternate syngas components

NexTech Sensor Development
Task 2.1.2 Hydrogen Sulfide Sensors

- Metal oxide based chemi-resistor (not electrochemical sensor) exhibits reversible and quantitative response to H_2S



- NexTech is currently evaluating various dopant schemes to reduce the temperature of operation
- Beta prototypes scheduled for early June

NexTech Sensor Development

Task 2.1.2 Hydrogen Sulfide Sensors

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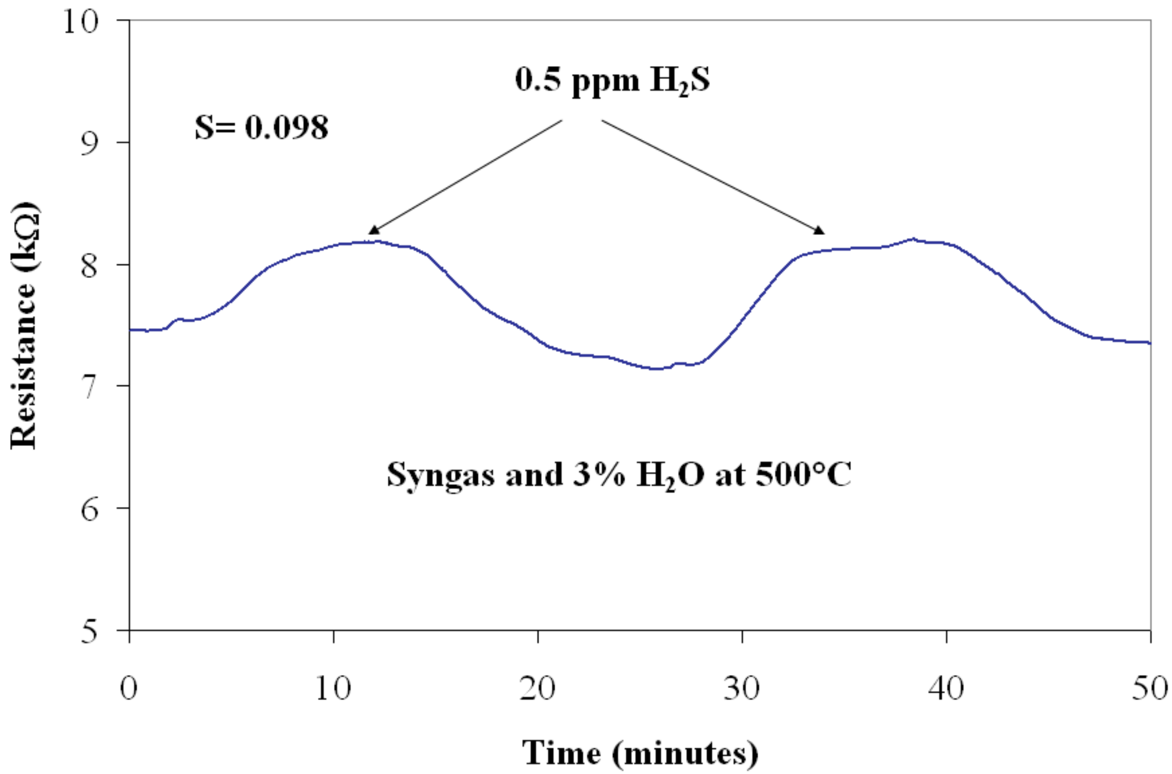
- Metal Oxide films show reversible response to H_2S concentrations at 0.5 ppm in syngas (goal of 0.05 – 0.5 ppm).



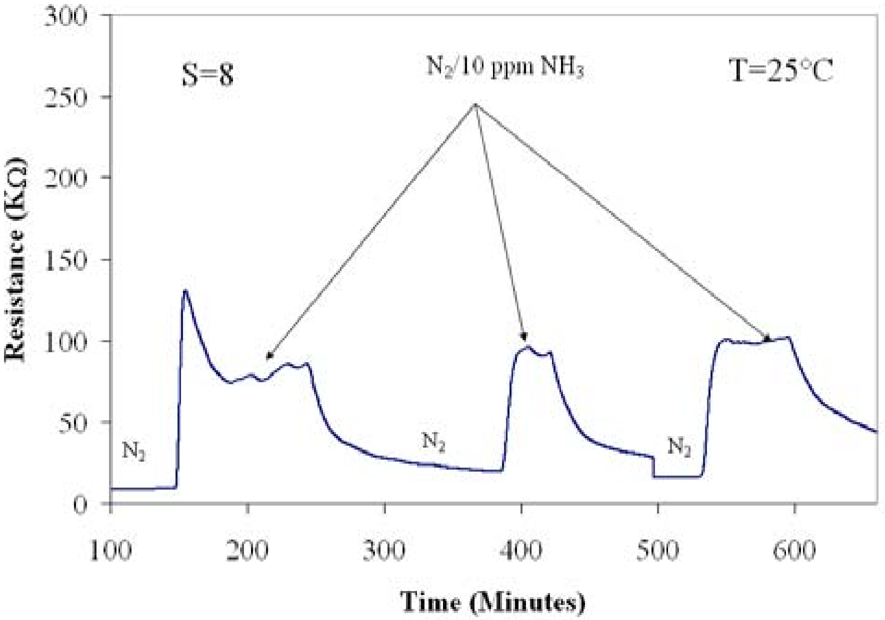
- Future work will focus on measuring lower sulfur concentrations and cross-sensitivity to individual syngas components.

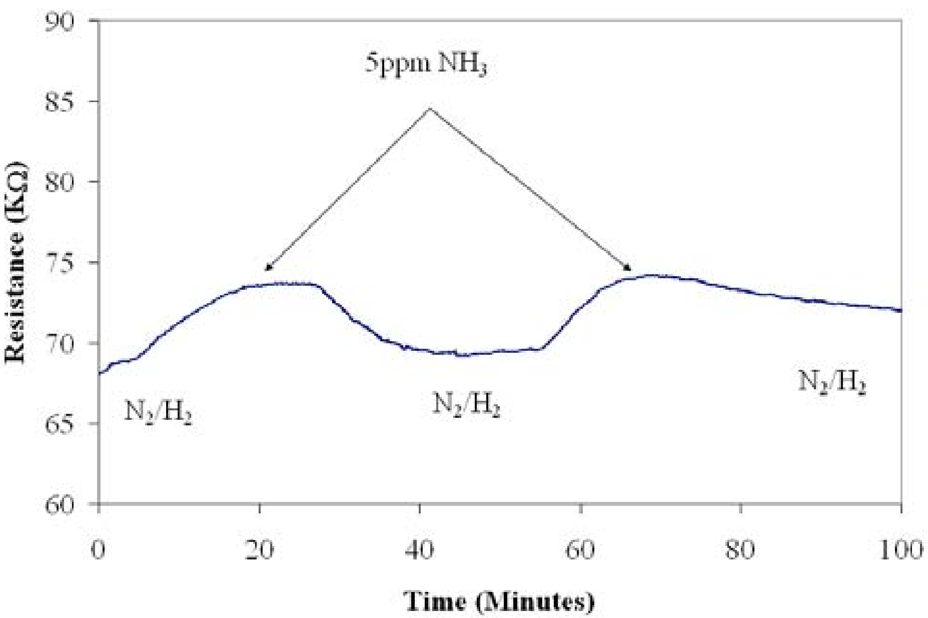
NexTech Sensor Development

Task 2.1.3 Ammonia Sensor Response

NEXTECH MATERIALS

NexTech's metal halide ammonia sensor shows very high sensitivity at low temperature





Sensor responds reversibly in N_2/H_2 at 75°C

Future work will focus on improving high temperature sensitivity and measuring cross-sensitivity to other syngas components.

Responses to Previous Year Reviewers' Comments

- "..difficult to assess technical approach and progress"
  - Physical sensor evaluation completed
  - H_2 LEL sensor developed
    - Best response times <1 s, average ~14s; sensor drift rate < 0.16% / day
  - Stack H_2 sensor developed
    - Dynamic response up to 40% H_2, H_2 levels up to 70%, with humidity
    - Fast response (T_{90}<2 sec) with Pd
    - New devices shows promise; minor cross sensitivity with CO; Drift <0.2% in 4% H_2
  - Multiple strategies identified for sensing CO in reducing environments; CO sensitivity established in humid environments
  - Multiple strategies for sulfur
    - ATMI- 50 nm Metal Foil shows response to H_2S
    - NexTech
      - H_2S/SO_2 sensor materials identified
      - PPM level detection demonstrated
  - Ammonia sensor easily packaged in a chemi-resistor format

Sensors for Automotive PEM-based Fuel Cells Project

Team organization

UTC Fuel Cells
A United Technologies Company

United Technologies
Research Center

DOE program manager and technical advisor:

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